A novel electrodeposition route for fabrication of the superhydrophobic surface with unique self-cleaning, mechanical abrasion and corrosion resistance properties

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ABSTRACT: Inspired by the adhesive proteins in mussels, a novel electrodeposition route has been developed to create multifunctional zinc (Zn)/ polydopamine (pDop)/ n-dodecyl mercaptan (NDM) composite coatings on different substrates, where oxidative polymerization of dopamine was simultaneously integrated during electrodeposition process. Hierarchical cauliflower-like structure was obtained on the electrodeposited Zn/pDop coatings. After modification with NDM, the prepared Zn/pDop/NDM coatings on different substrates (steel, Al and Cu) possessed excellent superhydrophobicity, exhibiting a maximum water contact angle (WCA) of 167.6° and a sliding angle (SA) less than 1° on the steel substrate. Scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS), Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) were employed to investigate the morphology and the chemical composition of the coatings. The mechanisms of electrodeposition process were discussed. The integrated electrodeposition and polymerization processes promised a synergistic effect on promoting the superhydrophobicity of coating. Results indicated that the dopamine greatly improved the mechanical abrasion resistance of the prepared superhydrophobic coatings. Additionally, these coatings demonstrated superior superhydrophobic stability, corrosion resistance and self-cleaning properties. It is believed that this novel and facile electrodeposition route for fabricating superhydrophobic coatings on various metallic materials will generate great impacts in practical applications.

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1. Introduction

Steel, aluminum and copper are widely used as engineering metal materials based on their unique characteristics of low-cost, high mechanical strength and good electrical/thermal conductivity [1-3]. However, corrosion and rusting cause enormous resources wastes and economic loss. Various strategies have been developed to regulate metal corrosion, such as cathodic protection [4], electrochemical etching [5], fabrication of protective coatings [6-7], etc. In recent years, inspired by the natural self-cleaning lotus leaf and the wings of butterflies, fabrication of superhydrophobic coatings has been applied in various engineering metal surfaces such as steel, aluminum, copper, magnesium and zinc, to realize the protection purpose because they can suppress the contact of a metal surface with water and corrosive medium from the environment [8, 9].

Up to now, various methods have been developed for fabricating superhydrophobic surfaces on metal substrates, such as chemical vapor deposition [10], sol-gel processing [11, 12], electrospinning [13, 14], chemical etching [15, 16] and anodic oxidation [17]. Nevertheless, most of these methods usually require special devices, complicated conditions, small substrate size and simple shape, limiting their widespread industrial applications.

Electrodeposition has been considered as a promising technique to construct large area superhydrophobic surfaces taking advantage of its simplicity, easy control, low-cost and suitability for practical applications [18-20]. Some researchers have prepared superhydrophobic surfaces with stable micro and/or nanoscale structures via electrodeposition. For instance, Haghdoust et al. [21] used a two-step electrodeposition technique to produce a superhydrophobic copper coating with a water contact angle of $160 \pm 6^\circ$ and sliding angle of $5 \pm 2^\circ$. In 2015, Li et al. [22] developed hierarchical structures with micro-flowers and secondary nano-sheets through electrodeposition. After fluorination, an excellent self-cleaning and superamphiphobic surface was obtained. Recent

studies demonstrated that electrodeposited superhydrophobic surfaces could achieve outstanding superhydrophobicity, self-cleaning and corrosion resistance properties. Unfortunately, to the best of our knowledge, the abrasion resistance and bonding strength of superhydrophobic surfaces have been rarely investigated in literatures. In fact, the industrial applications of superhydrophobic surface are greatly restricted by its poor mechanical properties and low adhesion strength. Some superhydrophobic coatings are even fragile to the finger-wipe and easily peeled off from substrates with mild abrasion. Hence, excellent mechanical abrasion resistance and strong adhesion to substrate are crucial factors to achieve practically useful superhydrophobic coatings.

In nature, marine mussels as a kind of promiscuous fouling organisms can easily attach to virtually all types of substrates by secreting *Mytilus edulis* foot protein-5 (Mefp-5) [23-24]. Further studies revealed that the adhesive proteins are rich in catecholic analogues (3, 4-dihydroxy-phenylalanine, DOPA), which can form strong covalent and noncovalent bondings on substrates [25]. According to Lee et al. [26], dopamine mimics the repetitive catechol-amine structure of DOPA, which can self-polymerize and deposit on numerous material surfaces in mild environment, and therefore its polymeric form (polydopamine) can be used as an efficient mechanical reinforcing agents. Recent investigations have found that divalent cations such as Cu^{2+} , Ni^{2+} , and Zn^{2+} can act as oxidants to polymerize dopamine, promoting the formation of adhesive melanin films [27]. Surprisingly, dopamine can also serve as an effective reducing agent to promote the electrodeposition process of metals. Hence, if the oxidative polymerization of dopamine and electrodeposition of metal can be processed simultaneously, this technique would open a new approach to construct functional superhydrophobic surfaces. Despite the unparalleled capability of dopamine, the application of dopamine in the electrodepositing system remains unexplored.

In this paper, a new route was developed to fabricate superhydrophobic coatings on steel, aluminum (Al) and copper (Cu) substrates. It was achieved by simple electrodeposition process on these substrates with both zinc ions and dopamine in the electrolyte solution. The influence of the

electrodeposition parameters including time and voltage on the wettability of the coatings was investigated. Additionally, the prepared superhydrophobic coatings achieved excellent anti-abrasion, anti-corrosion and self-cleaning properties. Therefore, it is expected that this research will pave a new way to design superhydrophobic functional coatings for the industrial application.

2. Experimental

2.1 Materials and reagents

Cu (T2), Al (1100) and steel sheet (Q235B) were obtained from Qingyuan Metal Co., China. The dimensions of these samples were 60 mm × 12 mm × 1 mm. N-dodecyl mercaptan (NDM) was purchased from Shanghai Zhanyun Chemical Co., Ltd. Dopamine was provided by Suzhou Tianke Trade Co., Ltd. Anhydrous ethanol, acetone, zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), potassium chloride (KCl), hydrochloric acid (HCl), nitric acid (HNO_3) and sodium chloride (NaCl) were all analytical grade and used without further purification. Deionized (DI) water with a resistivity greater than 18.0 M Ω ·m was used.

2.2 Modification of metal substrate

The steel sheets were abraded with successive grades of SiC paper from 400 to 1200 grade. After that, steel substrates were degreased in a mixture of ethanol and acetone (v/v: 1/1) for 15 min under sonication, then thoroughly washed by DI water. In addition, steel sheets were polished in 7 mol/L HCl solution for 1 h, then rinsed thoroughly with distilled water and dried under atmospheric conditions. The surface treatments of Cu substrates were first abraded and rinsed, similar to the steel sheets. Then the Cu substrates were etched in 3 mol/L HNO_3 solution for 5 min to create a rough structure. The Al substrates were polished with SiC paper (from 400 to 1200 grade) and used without further treatment.

2.3 Preparation of Zn/pDop/NDM coatings

As shown in Fig. 1, the superhydrophobic Zn/pDop/NDM coating with hierarchical micro/nano structure was obtained in the following processes. The electrodeposition process was

performed in a two-electrode electrochemical cell with a pre-treated substrate as cathode and a Cu plate as anode. The distance between the cathode and the anodic plate was fixed at 2 cm. ZnSO_4 (0.02 mol/L), KCl (0.1 mol/L) and dopamine (0.0065 mol/L) dissolved in distilled water was used as electrolyte. The solution pH was about 6.0 due to the addition of ZnSO_4 and was not readjusted. The electrodeposition temperature was kept at 40 °C. After electrodeposition process, the cathode specimens were removed from the solution and heat treated at 180 °C for 1 h in air. Finally, the samples were immersed in 0.25 mmol/L NDM anhydrous ethanol for 24 h at room temperature. Then the samples were taken out and adequately cleaned in anhydrous ethanol, followed by drying at room temperature.

2.4 Surface characterization

The surface wettability of the coatings was measured by contact angles (CAs) and sliding angles (SAs) with 5 μL liquid droplets using a contact-angle meter (JGW-360A, Chengdeshi Shipeng Detection Equipment Co., Ltd) at room temperature. In order to evaluate the hydrophobicity and oleophobicity of the coatings, the variations of CAs of water and glycol were investigated. The CAs reported were averages of three measurements per specimen. The surface morphologies of the prepared coatings were characterized by a scanning electron microscope (SEM, ZEISS, Germany). Fourier transform infrared (FT-IR) measurement was conducted using the Tensor 27 spectrometer with a 4 cm^{-1} resolution. The crystal structure of the coating was examined using X-ray diffraction (XRD, D/max2200). The elemental species of the samples were determined by energy-dispersive X-ray spectroscopy (EDS) using an Oxford Instruments X-Max 80 mm 2 silicon drift detector.

The adhesive performance of the substrates was obtained according to ASTM standard D3359-02 cross cut tape test. The coatings were scribbled into 1 mm $\times$ 1 mm gridding using a razor to expose the metal substrate, and then adhesive tape was pressed and pulled to separate coating from the scored metal surface.

The wear-resistant ability of the coatings was characterized by an abrasion test. The prepared surface was dragged to move on a rough cleaning cloth in one direction at a speed of $4\text{--}5\text{ mm}\cdot\text{s}^{-1}$ and a pressure of 2.8 kPa. The corrosion resistance of the coatings was investigated using the electrochemical workstation (LK 2010) in 3.5 wt.% NaCl solution, with Pt wire and saturated calomel electrode (SCE) as counter electrode and reference electrode, respectively.

3. Results and discussion

3.1 Surface morphology

Fig. 2 displays the SEM images of the polished steel and the electrodeposited surfaces before and after heat treatment. The morphologies of the electrodeposited coatings on the Cu and Al substrates are shown in Fig. S1. From SEM result (Fig. 2a), some scaly-like scratches were distributed on the surface of etched steel. Using the preprocessed steel sheet as substrate, the surface of the coating was covered by countless spherical nanoparticles after electrodeposition, as shown in Fig. 2b. Large amount of spherical particles with average diameter of 100 nm were gathered together to form dozens of larger-sized domains (Fig. S2b). Interestingly, the morphology of the coating was altered significantly after heat treatment. Large aggregated particles were converted to smaller rough grains and small particles were formed, due to the recrystallization and the increase of crystallinity during the heating process, as shown in Fig. 2c, d. It can be observed that the particles were feathered with average diameter from 20 to 50 nm, petal shaped and rough surface. These nano particles constituted numerous cauliflower-like microclusters, creating the hierarchical micro/nano structure of the superhydrophobic surface. The hierarchical rough structure created many channels where massive amounts of air can be stored and thus lead to the improvement of coating superhydrophobicity.

3.2 Coating composition and crystalline structure analysis

The EDS and FT-IR were utilized to characterize the chemical composition of the prepared coatings. On the basis of the chemical compositions of zinc sulfate and dopamine in the electrolyte

solution, the Zn, O and N elements were found in the prepared coating (Fig. 3a). The S element could also be found in the EDS spectrum due to the modification of NDM.

The FT-IR spectra of dopamine, pure substrate, Zn/NDM and Zn/pDop/NDM coatings are shown in Fig. 3b. Compared with the FT-IR spectra of dopamine, the Zn/pDop/NDM coating displayed similar peaks as dopamine at 1496 cm^{-1} , 1267 cm^{-1} and 809 cm^{-1} , corresponding to the stretching vibration of C=C, bending vibration O–H in aromatic ring and the bending vibration of N–H [28]. All the characteristic peaks indicated that the substrate was successfully coated by pDop. In the FT-IR spectra of Zn/NDM and Zn/pDop/NDM coatings, the peaks observed at 2922 cm^{-1} and 2878 cm^{-1} were attributed to the stretching vibrations of $-\text{CH}_3$ and $-\text{CH}_2-\text{S}$ of NDM [29]. A characteristic peak at 1051 cm^{-1} (C–S–C group) was also observed in Zn/pDop/NDM, confirming the successful assembling of NDM molecules coating on the prepared coating.

The XRD patterns of the pure substrates, the deposited Zn coatings before and after heat treatment are shown in Fig. 4. In Fig. 4a, the two characteristic peaks at $2\theta = 44.8$ and 65.1° can be indexed to Fe (110) and Fe (200) (PDF No. 87-0722). After electrodeposition, the diffraction peaks for Fe became weaker. At the same time, new peaks of Zn and ZnO were formed at $2\theta = 36.6, 38.9, 43.5, 65.1$ and 70.6° , corresponding to the crystal faces of ZnO (101) (PDF No. 79-2205), Zn (100) (PDF No. 87-0713), Zn (101), Zn (102), Zn (110) and Zn (110), Fig. 4a(ii). Applying a heat treatment process on the coating at 180°C for 1 h, a new diffraction peak at $2\theta = 55.6^\circ$ appeared ascribing to ZnO (110) (PDF No. 79-2205). The peak at $2\theta = 36.6^\circ$ became more distinct and sharper, indicating the structural transformation into more crystallized forms. As for the Al substrate, the peaks at $2\theta = 38.4, 44.7, 64.9$ and 78.4° are attributed to Al (111) (PDF No. 85-1327), Al (200), Al (220) and Al (311) (Fig. 4b). Two new peaks at $2\theta = 43.2$ and 70.6° appeared after electrodeposition, which corresponded to the Zn (101) and (110) crystal faces. After heat treatment, new peaks of Zn (100), Zn (110), ZnO (101) and ZnO (110) appeared, which further confirms the

positive contribution of heat treatment on promoting crystallization. Similar crystallization phenomena was also observed on Cu substrate, Fig. 4c.

3.3 Wettability of the sample surface under different conditions

To have a better understanding on the formation mechanism of the superhydrophobic Zn/pDop/NDM coatings, the CAs of water and glycol were measured on the coatings prepared from different processing conditions (Fig. 5). On the polished steel, the CAs of water and glycol were 74.7 and 61.4° respectively, Fig. 5a. The CAs of water and glycol increased to 91.7 and 79.8° after grafting NDM on the polished steel. These results indicated that the low-surface-energy molecules are able to enhance the hydrophobicity and oleophobicity of the solid surface. Once the Zn/pDop coating was deposited on the polished steel, the CAs of water and glycol reduced to 10.5 and 4.3°, which were even lower than those of polished substrates. The low CAs should be attributed to the adsorption of thin water films on the coating surface that restricted the capture of air in the rough structure. Besides, the abundant hydrophilic groups on the surface of the Zn/pDop coating resulted in its superior hydrophilicity and lipophilicity. However, the CAs of water and glycol increased to 115.3 and 109.9° after heat treatment due to following two reasons. Firstly, heat treatment removed the adsorbed water film in the coating. Secondly, the hierarchical micro/nano structure with trapped air was formed in the course of heating that effectively decreased the contact area between droplets and the solid surface. Therefore, thermal treatment is also a crucial factor to achieve the hydrophobicity of the coating. A further step of surface modification by NDM on the Zn/pDop coating reached even higher CAs of water and glycol up to 167.6 and 154.7°.

In this work, the Zn/pDop/NDM coatings were also applied to other metal substrates for the implementation of metal protection. Influence of processing conditions on the CAs of water and glycol of the Zn/pDop/NDM coatings on the Al and Cu substrate were similar to that of steel substrate (Fig. 5b, c). The WCAs of the Zn/pDop/NDM coatings on the Al and Cu substrates reached up to 166.5 and 164.9°, both realizing superhydrophobic surface feature.

3.4 The effect of various electrodeposition voltages and times

Electrodeposition voltage and time are key factors that influence the nucleation and growth processes of crystals and thus affect the surface morphology and wettability of the coatings. In this work, the effect of electrodeposition voltage and time on WCAs was investigated.

Previous research reveals that the voltage represents the driving force of the electrodeposition reaction [30], which means that the reaction extent of Zn electrodeposition and dopamine polymerization could be affected by the applied voltage. Fig. 6 displays variations of WCAs of the prepared surface under different deposition voltages for 30 min. Taking the steel supported coatings as an example, the WCAs gradually increased from 148.9 to 167.6° and then remained stable with increasing voltage from 0.5 to 2.5 V. Obviously, the surface morphology changed with applied voltage, which was revealed by the SEM results as illustrated in Fig. S3. By increasing voltages, the crystal grains grew bigger and new superfine particles were observed covering on the surface. When the voltage reached 1.5 V, the crystal grains were interconnected to form larger agglomerates (Fig. S3c), and the hierarchical micro/nano structure was constructed. Under this condition, the surface exhibited optimal superhydrophobicity with a maximum WCA of 167.6° and a minimum SA of 0.9°. However, when the deposited voltage further increased to 2.0 and 2.5 V, electrolysis of water and formation of bubbles on electrode surface negatively impact the coating structure. As depicted above, a voltage of 1.5V was considered as the optimal electrodeposition voltage to obtain the best morphology and wettability. The variations of WCAs of the coating on the Cu substrate were similar to the steel specimen. While the electrodeposition rate was rather slow on the Al substrate when the voltage was low, leading to a WCA of 138.4° and a SA of 46.5°. Then hydrophobic property of the coating on the Al substrate increased gradually with the increasing voltage, and the maximum WCA of 166.5° was also obtained at a voltage of 1.5 V.

The wettability of the superhydrophobic surfaces with different electrodeposition times at a voltage of 1.5V was studied as well, Fig. S5. Results revealed that the WCAs of the resulting

surface on the steel substrate firstly increased from 128.4° to 167.6° with increasing deposition time from 10 to 30 min, and achieved the maximum value of 167.6° when the time was 30 min, finally it decreased to 155.1° when the electrodeposited time was 60 min. It was therefore revealed that the optimal electrodeposition time for fabricating superhydrophobic surfaces was 30 min.

3.5 Characteristics and Features of the superhydrophobic coatings

3.5.1 Self-cleaning characteristics

Self-cleaning property is crucial for superhydrophobic surfaces in practical applications. Fig. 7 demonstrates the testing process of self-cleaning properties of the prepared Zn/pDop/NDM coating on Cu substrate. Self-cleaning behavior of the prepared coatings on the other two substrates were also discussed (in Fig. S6, S7). As shown in Fig. 7 (a1, a2, a3), the coated surface was immersed into the muddy water (mud content: 200 kg/m³) and maintained its clean surface without any contaminants even after 30 testing cycles. In Fig. 7 (b1, b2, b3), self-cleaning property of the superhydrophobic surface was also investigated by applying sand as contaminants to the surface. After dropping sand on the coating surface, all sand could be easily washed away by water. The outstanding self-cleaning property can be explained by the joint action of the hierarchical rough structures and low-surface-energy materials. On the one hand, the hierarchical rough structures trapped the air, which could efficiently restrain the contact of the dirt with surface. On the other hand, the introduction of NDM decreased the surface energy of the as-prepared coatings, which further prevented the infiltrating of liquid into the coating. It is worthwhile to mention that the sand and mud used in these experiments were far more critical than those in most application environments, while the prepared Zn/pDop/NDM coatings still showed excellent self-cleaning and anti-fouling properties.

3.5.2 Mechanical stability of the prepared coatings

Mechanical strength of the coating is critical in practical applications. In this study, the mechanical strength was evaluated in terms of the adhesive and anti-wear properties of the prepared

coatings. Cross cut tape test of these coatings on the substrates was conducted according to the ASTM standard D3359-02 to investigate the adhesion of the coating to substrate. Fig. 8 shows the diagram of the superhydrophobic surfaces before and after the tape tests on the (a) steel, (b) Al and (c) Cu specimen. The superhydrophobic coatings demonstrated excellent adhesion without any squares peeled off from the substrate after the cross cut tape test. Notable traces were not detected on the adhesive tapes after pull and removal of the tapes. Moreover, the Zn/pDop/NDM coatings still exhibited high water repellency after the tape test. The superior interfacial strength between the Zn/pDop/NDM coatings and substrate was mainly attributed to the incorporation of adhesive dopamine. Oxidative polymerization of dopamine was used to form strong metal bonds with Zn crystals and metal substrates and further developed thin surface-adherent polydopamine films between Zn coatings and substrates under the action of electricity and heating [31]. This codeposition process can significantly increase the binding strength between the Zn/pDop coatings and substrates. Additionally, polydopamine can also form covalent bond with NDM to achieve excellent chemical stability of the superhydrophobic surfaces.

A robust surface, as a crucial property of coating's application, has a direct impact on maintaining surface function and durability in practical applications. In order to verify the role of dopamine in the coating, the abrasion tests for the Zn/pDop/NDM and Zn/NDM coatings were comparatively studied. Fig. 9a shows the schematic diagram of the abrasion test. In this work, a rough cleaning cloth was used as an abrasion surface in the abrasion test, which can fully contact with surfaces and better evaluate the adhesive strength between the coating and substrate. The prepared coatings were placed face-down to the cleaning cloth and dragged to move at a speed of 4-5 mm·s⁻¹ and a pressure of 2.8 kPa. The WCAs after abrasion for a certain length of the coatings are shown in Fig. 9 (b, c). It can be found that the surface of the Zn/NDM coating was severely damaged and the WCA decreased from 161.1° to 103.2° after 600 mm abrasion (Fig. 9b). The Zn/NDM surface superhydrophobicity can only remain within an abrasion distance of 100 mm. However,

the WCA of the prepared Zn/pDop/NDM coating still remained above 150° and the SA less than 10° after abrasion for 500 mm, indicating superhydrophobicity was slightly damaged by mechanical abrasion. When the abrasion length increased to 600 mm, the WCA of the Zn/pDop/NDM coating decreased to 147.9° and the SA increased to 12.9° (Fig. 9c). The Zn/pDop/NDM coating showed strong mechanical abrasion resistance, which was also much better than other reported superhydrophobic coatings [32-34]. For instance, Liu et al. prepared a ZnO nanorod/epoxy composite film can only endure an abrasion length of 250 mm [32]. In 2014, Li et al. reported a superhydrophobic surface fabricated via electrochemical method can only maintain the CAs above 150° after abrasion 400 mm under a pressure of 1.2 kPa [33].

The enhanced wear resistance of the Zn/pDop/NDM coating can be mainly attributed to the high bonding strength between the NDM molecules and the Zn/pDop coated surface. Research showed that catechols or o-quinone can react with thiols via Michael addition reactions under oxidative conditions [26]. Thus NDM was grafted on the Zn/pDop/NDM surface and formed C-S-C covalent bond with polydopamine. As for the Zn/NDM coating, NDM molecules were physically adsorbed on the Zn coating surface. This study proves that chemically bounded NDM coating provided superior chemical stability that of the coatings with physical absorption.

Fig. 9 (d1, d2) shows the optical images of abrasion trace on the coatings after abrasion test. Zn/NDM coating shows obvious abrasion trace after the friction test, Fig.9 d1. In contrast, the surface of the Zn/pDop/NDM coating remained undamaged, which proved that the Zn coating was strongly adhered to the substrate by incorporating the adhesive dopamine. Therefore, such Zn/pDop/NDM coatings showed improved mechanical abrasion resistance.

3.5.3 Chemical stability and anticorrosion properties

Fig. 10 (a1, a2, a3) shows the effect of solution pH value on the wettability of the prepared Zn/pDop/NDM coatings on different substrates. Obviously, all of the WCAs were above 158° even at pH=1 and pH=14, which illustrated that the prepared coatings can retain superhydrophobicity in

extremely environment such as strong acid and alkali environments. In most studies, the superhydrophobic coatings fabricated by electrodeposition method could not survive in strong acidic environment [35, 36]. In extreme environments, metals coatings are ready to react with acid and the coarse surface structure can be easily damaged. Besides, the low surface energy materials on the surface will be dissolved and lose its functionality. In this work, zinc crystals coated with polydopamine can effectively protect the surface from being destroyed. Moreover, the modifier NDM can form strong covalent bond with polydopamine of the surface, achieving the better chemical stability of the Zn/pDop/NDM coatings.

In order to further evaluate the corrosion protection of the coatings, the Tafel plots for the pure substrate and the Zn/pDop/NDM coatings were characterized (Fig. 10b1, b2, b3). Corrosion potential (E_{corr}) and corrosion current density (I_{corr}) obtained by Tafel extrapolation method directly reflect the electrochemical corrosion resistance (Table 1). Typically, positive E_{corr} represents lower thermodynamical corrosion tendency and smaller I_{corr} value means lower corrosion dynamic rate [37]. As for the steel substrate, the E_{corr} of the superhydrophobic Zn/pDop/NDM coating positively shifted from -695.1 to -580.9 mV. The I_{corr} of the pure steel sheet was 3.6×10^{-1} mA/cm², while the I_{corr} of the coating was 4.8×10^{-2} mA/cm² (Fig. 10b1). As shown in Fig. 10b2, the E_{corr} and the I_{corr} of the pure Al were -825.8 mV and 5.1×10^{-2} mA/cm². While after superhydrophobic treatment the E_{corr} and the I_{corr} were -674.4 mV and 5.5×10^{-3} mA/cm², respectively. As expected, the increase in E_{corr} and the decrease in I_{corr} confirmed that the prepared coatings had better corrosion resistance than the pure steel and Al substrates. Fig. 10b3 shows the Tafel plot of the pure Cu sheet and the corresponding coatings. Owing to the specific characteristics of the Cu substrate, the E_{corr} of the Cu sheet reached a relative high value of -109.8 mV, while the slight shift to a more negative value of the prepared coating. On the contrary, the superhydrophobic surface exhibited a very low corrosion rate, a 64-fold decrease from the pure Cu substrate. The lower I_{corr} is consistent with the better

corrosion resistance. The above results indicated that the prepared Zn/pDop/NDM coatings obtained excellent anti-corrosion property in harsh corrosive environment.

Possible interface model and anticorrosion mechanism of the superhydrophobic surface were proposed here. An illustration for anticorrosion mechanism of different specimens in corrosive medium is presented in Fig. 11. When the pure substrate was immersed in the corrosive medium, the medium directly contacted with substrates and corrosive chloride ions could easily permeate through the thin passivation film, resulting in serious erosion of metals. After coating the superhydrophobic Zn/pDop/NDM layer, the hierarchical micro/nano structures formed on the surface encompassed lots of grooves filled with air. Thus, the corrosive medium are not able to wet the superhydrophobic surface according to the Cassie–Baxter model [38]. When the prepared coating was immersed in the corrosive medium, the trapped air in the groove of hierarchical structure could also block the contact of corrosive media with the substrate and generated a better anti-corrosion property.

3.6 Mechanism of electrodeposition process

Based on the chemical composition and surface structure mentioned above, the possible growth mechanisms of the coating during the electrodeposition process were proposed as follow (Fig. 12). When the DC voltage was used in the electrodeposition system, Zn^{2+} ions around the cathode plate received electrons, and then Zn nucleus appeared on the cathodic surface. Due to the addition of zinc sulfate, the pH of the solution was about 6.0 at the beginning of the reaction. Thus hydrogen ions also captured electrons around the cathode plate and released hydrogen. More Zn nucleus generated and grains grew gradually on the surface in the electrodeposition process. Meanwhile, polymerization of dopamine was also conducted in the system of electrodeposition. Some of the polydopamine deposited and adhered to the cathode surface. Another part of the adhesive polydopamine molecules anchored on Zn nucleus and co-deposited with Zn on the substrates. The synthesized polydopamine as a kind of binding agent between deposited Zn and

substrates can effectively improve the adhesive strength at the interface. The pH of the electrolyte solution continuously decreased during the electrodeposition process. When the electrodeposition process was completed, the solution pH decreased to 5.0. Part of copper was dissolved and formed blue-green $\text{Cu}(\text{OH})_2$ film on the anode plate.

The polymerization process of dopamine is shown in Fig. 12. Firstly, large amounts of dopamine were oxidized to dopamine-quinone. Then, leucodopaminechrome was generated through intramolecular cyclization and oxidation. Reaction products may be converted to the 5, 6-dihydroxyindole in the isomerization and further oxidized to 5, 6-indolequinone [27]. The oxidative polymerization of dopamine can be accelerated under the action of electricity and heating during electrodeposition. Surprisingly, we found Zn^{2+} in the electrolyte could also promote the oxidative polymerization. Research reported that divalent cations such as Zn^{2+} , Ni^{2+} and Cu^{2+} can act as oxidants in the polymerization of dopamine, directing the oligomerization of 5, 6-dihydroxyindole to the formation of 2, 2' dimers [39]. Thus dopamine can be deposited even in the acid electrolyte under the oxidation of Zn^{2+} . In addition, dopamine can also play a role as an effective reducing agent due to its oxidative polymerization to produce polydopamine (pDop), which can promote the electrodeposition of Zn coatings. In consequence, the processes of self-polymerization and electrodeposition can realize mutual promotion in the whole system by our particular experimental design.

4. Conclusions

In summary, we have successfully fabricated novel, multifunctional superhydrophobic coatings with hierarchical cauliflower-like structure on various metal substrates by the simple processes of electrodeposition and chemical grafting. Results indicated that when the electrodeposited voltage was 1.5 V and the time was 30 min, all of the Zn/pDop/NDM coatings on the steel, Al and Cu substrates have shown the optimal superhydrophobic property with the maximum WCAs exceeding 160° and SAs less than 1° . Based on the superior wettability, the

Zn/pDop/NDM coatings had outstanding self-cleaning property, corrosion resistance and chemical stability in various pH conditions. They can be used in both acidic and alkaline conditions. Besides, the Zn/pDop/NDM coatings exhibited improved mechanical abrasion resistance and adhesive strength due to the unrivalled adhesion of polydopamine. We believe this novel route to fabricate superhydrophobic coatings will generate large impact in practical applications, including superhydrophobic surface, self-cleaning, anticorrosion and antiabrasion materials.

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Figure captions

Fig.1. Scheme of the preparation process of Zn/pDop/NDM coating.

Fig.2. SEM images of (a) polished steel, steel substrate coated with a Zn/pDop coating (b) before and (c, d) after heat treatment. [Insert \(d\): An optical image of a cauliflower.](#)

Fig.3. Chemical composition analysis of the Zn/pDop/NDM coating: (a) EDS and (b) FT-IR.

Fig.4. XRD patterns of the (i) pure substrates and Zn/pDop coated surfaces (ii) before and (iii) after heat treatment on the (a) steel, (b) Al and (c) Cu sheet.

Fig.5. CAs of water and glycol on the (a) steel, (b) Al and (c) Cu substrate under different processing conditions. (d) Optical images of water and glycol droplets on the substrates and Zn/pDop/NDM coatings.

Fig.6. Variation in the WCAs and SAs of the coatings on the (a) steel, (b) Al and (c) Cu substrate obtained at different electrodeposition voltages.

Fig.7. Self-cleaning effect experiments: (a1,2,3) Zn/pDop/NDM coating immersed into the muddy water. (b1) Zn/pDop/NDM coating dusted with sand, (b2) Zn/pDop/NDM coating cleaned with distilled water, (b3) sand completely removed from the coating.

Fig.8. Optical images of the Zn/pDop/NDM coatings (a) before and (b) after the cross cut tape test.

[Insert figure is the water contact angle.](#)

Fig.9. (a) Schematic diagram of the abrasion test; Influence of the abrasion on the wettability of the (b) Zn/NDM and (c) Zn/pDop/NDM coatings on the steel substrate; Optical images of abrasion trace on the (d1) Zn/NDM and (d2) Zn/pDop/NDM coatings after abrasion test.

Fig.10. Effect of solution pH on the superhydrophobicity of the coatings on the (a1) steel sheet, (a2) Al sheet and (a3) Cu sheet. The Tafel plots for the pure substrates and Zn/pDop/NDM coatings on the (b1) steel substrate, (b2) Al sheet and (b3) Cu sheet.

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Fig.12. Schematic diagram of the electrodeposition process.

Figures

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Steel	<p>167.6° 1mm×1mm</p> <p>After cross cut tape test → (a)</p> <p>Tape 163.5°</p>
Al	<p>166.5°</p> <p>After cross cut tape test → (b)</p> <p>158.9°</p>
Cu	<p>164.9°</p> <p>After cross cut tape test → (c)</p> <p>160.4°</p>

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Table 1 Corrosion potentials (E_{corr}) and corrosion current densities (I_{corr}) of the substrates and superhydrophobic Zn/pDop/NDM coatings

Specimen	Steel		Al		Cu	
	Substrate	coating	Substrate	coating	Substrate	coating
E_{corr} (mV)	-695.1	-580.9	-825.8	-674.4	-109.8	-231.9
I_{corr} (mA/cm ²)	3.6×10^{-1}	4.8×10^{-2}	5.1×10^{-2}	5.5×10^{-3}	7.7×10^{-1}	1.2×10^{-2}

Graphical abstract

A novel electrodeposition route for fabrication of the superhydrophobic surface with unique self-cleaning, mechanical abrasion and corrosion resistance properties

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